
Name of Organization: Health Research Inc. and New York State Dept. of Health

Type of Organization: State

Contact Information: Dr. G-Yull Rhee
Wadsworth Center, New York State Dept. of Health
P.O.Box 509, Empire State Plaza
Albany NY 12201

Phone: (518) 473 - 8035 **Extension:**

Fax: (518) 486 - 2697

E-Mail: rhee@wadsworth.org

Project Title: Microbial Detoxification of PCBs in Contaminated Sediments

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested (\$): 297,365 **Project Duration:** 2 Years

Abstract:

The primary use impairment of the St. Lawrence River at Massena AOC on the US side is largely due to PCB contamination from three industrial plants: the General Motors Foundry, Reynolds Aluminum, and ALCOA. In the absence of an effective remediation technology, the most common impairment restoration involves dredging and sequestration in a confined disposal facility (CDF). The most heavily-contaminated sediments near the GM site were dredged in 1998 for disposal at a site yet to be selected and dredging is also planned for the Reynolds site. However, such disposal is not a fundamental solution since it does not break down PCB molecules. The disposal of dredged sediments in a CDF actually prevents the natural dechlorination of PCBs, however slow or limited it may be, and contributes to preserving PCBs. Our recent study has revealed that the absence of PCB dechlorination, a critical first step in the biodegradation of highly chlorinated and recalcitrant congeners, was due to the moisture-limited death of dechlorinating microorganisms in dredged sediments. Our preliminary investigations have shown that various PCB dechlorinating microorganisms can be enriched by low molecular weight non-PCB haloaromatic compounds in PCB-contaminated St. Lawrence River sediments and the enrichment significantly enhanced PCB dechlorination. The goal of the present proposal is to develop bioremediation technologies for PCBs in dredged sediments in a CDF through selective enrichment of naturally occurring microorganisms capable of anaerobic dechlorination of recalcitrant congeners. The final dechlorination products will then be degraded through the enrichment of aerobic PCB-degrading microorganisms. This study will be carried out in a simulated CDF in the laboratory using PCB-contaminated sediments from the St. Lawrence River.

Geographic Areas Affected by the Project

States:

<input checked="" type="checkbox"/> Illinois	<input checked="" type="checkbox"/> New York
<input checked="" type="checkbox"/> Indiana	<input checked="" type="checkbox"/> Pennsylvania
<input checked="" type="checkbox"/> Michigan	<input checked="" type="checkbox"/> Wisconsin
<input checked="" type="checkbox"/> Minnesota	<input checked="" type="checkbox"/> Ohio

Lakes:

<input type="checkbox"/> Superior	<input type="checkbox"/> Erie
<input type="checkbox"/> Huron	<input type="checkbox"/> Ontario
<input type="checkbox"/> Michigan	<input checked="" type="checkbox"/> All Lakes

Geographic Initiatives:

☐ Greater Chicago ☐ NE Ohio ☐ NW Indiana ☐ SE Michigan ☐ Lake St. Clair

Primary Affected Area of Concern: St. Lawrence River, NY

Other Affected Areas of Concern:

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

To restore the unimpaired use of the St. Lawrence River at Massena AOC, dredging is being used as the method of choice due to lack of alternate technologies. Most of the heavily contaminated sediments were dredged from the GM site in 1998 for disposal at containment sites which have yet to be located. Dredging is also planned for the Reynolds site. However, this physical sequestration is only effective for the life of the containment facility and does not destroy the toxic agents themselves. Our investigations of over 20 year old PCB-contaminated dredged sediments from the Hudson River encapsulated at Moreau, NY, showed no sign of dechlorination even though the sediments at the dredged site in the river showed significant further degradation (Cho et al., 2000b). However, the physical containment in a CDF renders itself readily to ex situ treatments and therefore, with appropriate new technologies, it is possible to completely and permanently detoxify PCBs in this facility.

A crucial barrier limiting PCB biodegradation is the inability of aerobic microorganisms to breakdown highly chlorinated congeners. Therefore, the critical step in bioremediation of PCBs is to reduce the degree of chlorination of these congeners to a level where aerobic microorganisms can degrade and mineralize. Anaerobic PCB dechlorinating microorganisms can mediate this step through the preferential removal of chlorines from the meta and para positions. However, natural dechlorination in the St. Lawrence River seldom achieves the low level of chlorination required for aerobic biodegradation or mineralization. To reach this level, dechlorinating populations of diverse competence are needed to dechlorinate not only various parent congeners but also intermediate dechlorination products. However, some essential dechlorinator populations appear to be either absent or present in insufficient numbers in natural sediments (Sokol et al., 1998; Rhee et al., 2000; Cho et al., 2000b). Our preliminary studies have revealed that it is possible to selectively enrich dechlorinator of specific competence using simpler and less toxic haloaromatic compounds such as chlorobenzoates, chlorophenols and chlorobenzenes. We have also determined in laboratory studies that a crucial factor in preventing dechlorination in dredged sediments is the inhibition of dechlorinator growth by low moisture levels (Cho et al., 2000b). Based on these findings, we propose to develop bioremediation technologies for PCBs using selective enrichment of dechlorinating microorganisms for the anaerobic dechlorination of resistant congeners and for subsequent aerobic degradation of dechlorination products in a laboratory simulation of a CDF using PCB-contaminated sediments from the St. Lawrence River.

Proposed Work Outcome:

Background: A critical barrier to PCB bioremediation is the recalcitrance of highly chlorinated congeners to microbial degradation. Reductive dechlorination by anaerobic microorganisms in contaminated sediments can potentially eliminate this impediment by removing Cl's from the biphenyl ring. In freshwater sediments, dechlorinating microorganisms selectively remove chlorines from the meta- and para-positions. However, dechlorination in natural sediments in general is very slow, taking place over many years and the level of chlorination in many products is still too high for breakdown by

aerobic microorganisms. It appears that various dechlorinating populations are involved depending on the Cl substitution pattern on the ring and that the extent of dechlorination is determined by the availability of competent populations not only for existing congeners but also for their intermediate dechlorination products (Rhee et al., 1993; Sokol et al., 1994; Sokol et al., 1998; Kim and Rhee, 1999; Cho et al., 2000).

Efforts to develop dechlorination technology have been hampered by poor understanding of the microbiology of dechlorination, due largely to the failure to isolate responsible organisms. However, our recent investigations of St. Lawrence River sediments have shown that microbial dechlorination is tightly linked to the growth of dechlorinating populations and that these populations require PCBs for growth, probably as alternate electron acceptors (Kim and Rhee, 1997). Kinetic studies of PCB dechlorination have also shown that dechlorination rate is significantly correlated to growth rate (Rhee et al., 2000).

Our preliminary investigations show that PCB-dechlorinating microorganisms can be enriched by other haloaromatic compounds such as chlorobenzoic acids, chlorophenols, and chlorobenzenes in PCB-free sediments. With certain isomers of these compounds, the total number of PCB dechlorinators, as determined by the MPN technique, was greater than in PCB-spiked sediments. When these compounds were spiked into Aroclor 1248-contaminated sediments, PCB dechlorination was significantly enhanced compared to sediments with PCBs alone. More importantly, the results indicate that these compounds selectively enrich dechlorinating populations of different competence; for example, enrichment with various chlorobenzoate isomers, 2,3-, 3,4-, or 2,3,6-phenol, and 1,2- or 1,2,4-benzene resulted in a significantly higher meta dechlorination of various congeners compared to dechlorination in sediments with PCB alone. Similarly, enrichment with 1,2,3-benzene enhanced para dechlorination. Enrichment with 3-benzoate, 2,3-phenol and 1,2,4-benzene enhanced dechlorination at both meta and para positions. It is not surprising that PCB dechlorinators can grow on non-PCB haloaromatic compounds, since dehalogenating enzymes are not specific to a single compound (Gerritse et al., 1996; Sanford et al., 1996; Holliger et al., 1999). Other dehalogenating microorganisms are also capable of utilizing multiple substrates; for example, *Desulfitobacterium* sp., which was isolated from a tetrachloroethene-dechlorinating culture, is capable of dechlorinating tetrachloroethene and chlorophenols (Gerritse et al., 1996).

Recent investigations on dredged sediments and the effect of moisture on PCB dechlorination (Cho et al., 2000b) have shown that the extent of dechlorination increased with the moisture level and that the moisture-limited dechlorination is due to the moisture-dependence of growth of dechlorinating microorganisms. Therefore, the moisture content appears to be the most critical factor in sustaining and promoting dechlorination in dredged sediments.

Proposed Work: The proposed study will clearly define the selective enrichment characteristics of various isomers of chlorobenzoates, chlorophenols, chlorobenzenes, and other haloaromatic compounds (such as bromobiphenyls) for PCB-dechlorinating microorganisms and their specific dechlorination specificity. At the same time, it will also determine the minimum effective concentrations of these enrichment compounds and their degradation. Based on this information, we will develop techniques to enhance PCB dechlorination in dredged sediments from the St. Lawrence River through direct enrichment or the inoculation of enriched populations in a bench top CDF containing St. Lawrence River sediments with an optimization of the moisture content. The final dechlorination products will then be degraded through the direct enrichment by biphenyl of aerobic PCB-degraders or the inoculation of enriched populations and aeration (physical or chemical)

Outcome: The results of the present study will enable us to utilize a CDF not only for physical containment but also for the complete detoxification of PCBs well within its design life. Although this study is focused on the St. Lawrence River, the results can apply to the remediation of PCB-contaminated sediments at other sites in the Great Lakes areas and elsewhere. The results of this study are also equally applicable for the remediation of other haloaromatic compounds as well as mixtures of haloaromatic contaminants.

References

- Cho, Y.-C., J. Kim, R. C. Sokol, and G-Y. Rhee. 2000a. Biotransformation of PCBs in St. Lawrence River sediment: reductive dechlorination and dechlorinating microbial populations. *Can. J. Fish. Aquat. Sci.* In press.
- Cho, Y.-C., O.-S. Kwon, R. C. Sokol, C. M. Bethoney, and G-Y. Rhee. 2000b. Microbial PCB dechlorination in dredged sediments and the effect of moisture. *Chemosphere* In review.
- Gerritse, J., V. Renard, T. M. P. Gomes, P. A. Lawson, M. D. Collins, and J. C. Gottschal. 1996. *Desulfitobacterium* sp. strain PCE1, an anaerobic bacterium that can grow by reductive dechlorination of tetrachloroethene or ortho-chlorinated phenols. *Arch. Microbiol.* 165:132-140.

Holliger, C., G. Wohlfarth, and G. Diekert. 1999. Reductive dechlorination in the energy metabolism of anaerobic bacteria. *FEMS Microbiol. Rev.* 22:383-398.

Kim, J., and G-Y. Rhee. 1997. Population dynamics of polychlorinated biphenyl-dechlorinating microorganisms in contaminated sediments. *Appl. Environ. Microbiol.* 63:1771-1776.

Kim, J., and G-Y. Rhee. 1999. Interactions of polychlorinated biphenyl-dechlorinating microorganisms with methanogens and sulfate reducers. *Environ. Toxicol. Chem.* 18:2696-2702.

Rhee, G.-Y., B. Bush, C. M. Bethoney, A. DeNucci, H.-M. Oh, and R. C. Sokol. 1993. Reductive dechlorination of Aroclor 1242 in anaerobic sediments: pattern, rate and concentration dependence. *Environ. Toxicol. Chem.* 12:1025-1032.

Rhee, G.-Y., R. C. Sokol, C. M. Bethoney, Y.-C. Cho, R. C. Frohnoefer, and T. Erkkila. 2000. Kinetics of PCB dechlorination and growth of dechlorinating microorganisms. *Environ. Toxicol. Chem.* In review.

Sanford, R. A., J. R. Cole, F. E. Löffler, and J. M. Tiedje. 1996. Characterization of *Desulfotobacterium chlororespirans* sp. nov., which grows by coupling the oxidation of lactate to the reductive dechlorination of 3-chloro-4-hydroxybenzoate. *Appl. Environ. Microbiol.* 62:3800-3808.

Sokol, R. C., O.-S. Kwon, C. M. Bethoney, and G.-Y. Rhee. 1994. Reductive dechlorination of polychlorinated biphenyls (PCBs) in St. Lawrence River sediments and variations in dechlorination characteristics. *Environ. Sci. Technol.* 28:2054-2064.

Sokol, R. C., C. M. Bethoney, and G-Y. Rhee. 1998. Effect of Aroclor 1248 concentration on the rate and extent of PCB dechlorination. *Environ. Toxicol. Chem.* 17:1922-1926.

Project Milestones:**Dates:**

Project Start

09/2000

Enrichment and Dechlorination processes

09/2000

Anaerobic treatment of dredged sediments

09/2001

Aerobic treatment

05/2002

/

/

/

Project End

09/2002

☐

Project Addresses Environmental Justice

If So, Description of How:☒

Project Addresses Education/Outreach

If So, Description of How:

Education and outreach is an integral part of the project. Graduate students will carry out some parts of this study. (The PI is also Professor, School of Public Health, SUNY-Albany). The results of the proposed work will be shared with US EPA and NYS Dept. of Environmental Conservation, the lead agencies for developing and implementing the St. Lawrence River at Massena RAP. The information will also be distributed to the Nohaw Nation at Akwesasne which has jurisdiction over a large part of the AOC. Finally, the information will be disseminated through conference presentations and publications in peer-reviewed journals.

Project Budget:

	Federal Share Requested (\$)	Applicant's Share (\$)
Personnel:	127,514	52,000
Fringe:	29,238	13,520
Travel:	7,000	0
Equipment:	0	0
Supplies:	31,000	0
Contracts:	0	0
Construction:	0	0
Other:	4,900	0
Total Direct Costs:	199,652	65,520
Indirect Costs:	97,713	26,208
Total:	297,365	91,728
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

National Institute of Environmental Health Sciences. \$750,000 (April, 1995-March, 2001). This project investigates factors affecting PCB dechlorination, dechlorination kinetics, and in situ dechlorination in the St. Lawrence River.

US EPA. \$500,000 (Jan. 1997-Dec. 2000). This project studies the population dynamics of PCB dechlorinating microorganisms in the St. Lawrence River.

Description of Collaboration/Community Based Support:
